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THE EFFECT OF STRESS ON DIFFUSION IN COM-
POSITES - EXPERIMENTAL OBSERVATIONS

D. C. Ruhmann, et al

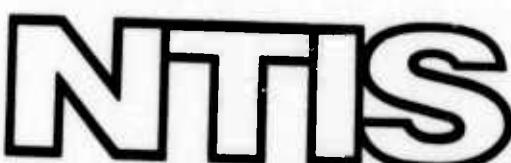
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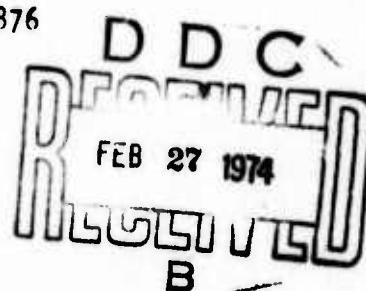
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13. ABSTRACT

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FOREWORD

The research reported herein was conducted by the staff of Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites".

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The Effect of Stress on Diffusion
In Composites - Experimental Observations

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This paper is concerned with the investigation of the effect of anisotropy on the sorption characteristics of benzene by a glass-epoxy (60% Epon 815-40% Versamid 140) composite system. The objective of this research is to characterize the effect of the unidirectional glass filaments at various orientations on the rate and mode of sorption and to establish the applicability of expressions of the form $F_i = D_{ij}C_{,j}$ where F_i is the flux and D_{ij} is a second order diffusion coefficient for describing diffusion in our composite system. A one-dimensional diffusion experiment was performed to establish the effect internal stresses have in modifying the sorption rate of the homogeneous epoxy matrix material. The research has revealed the presence of competing mechanisms which control the rate and mode of sorption by the composite system. The analysis of stress in the one-dimensional diffusion specimens using a finite element method (elastic solution) has shown an increase in the deviatoric tensile stress in the direction of the flux increases the rate of sorption.

THE EFFECT OF STRESS ON DIFFUSION
IN COMPOSITES - EXPERIMENTAL OBSERVATIONS

INTRODUCTION

A research program to investigate the effect of anisotropy on the sorption characteristics of benzene by a glass-epoxy composite material system was initiated. This program was begun in support of other research currently being conducted at Washington University to characterize the effect of solvents on the survival life of polymeric composites [1]. The purpose of the diffusion studies was to provide a deeper understanding of the mechanisms of sorption of organic solvents by composite materials and to provide insight into the effect the sorption kinetics may have in determining stress-rupture life.

This paper is concerned with the results of the above investigation. The work was conducted in three phases; the first being the characterization of the sorption of benzene by the homogeneous epoxy matrix; the second, an experimental study of the effect of anisotropy resulting from the unidirectional glass filaments on the sorption characteristics; the third, an experimental investigation into the role internal stresses generated as a result of the dilatation which accompanies the sorption of the organic solvent have in determining the response of the material system to the presence of the solvent.

The samples used in this study were prepared from homogeneous epoxy resin (60% Epon^R 815 - 40% Versamid^R by weight) sheets and rods and composite sheets having the epoxy resin as the matrix with unidirectional glass fiber-reinforcement.

EXPERIMENTAL

Sample Preparation:

The epoxy resin used in this study consisted of a mixture of 60% by weight Shell Epon^R 815 and 40% General Mills Versamid^R 140. Chemical reaction between the amino groups of the Versamid resin and the epoxide groups of the Epon 815 resin results in a cross-linked polymer. Mixing was conducted under vacuum to minimize the presence of voids. The isotropic sorption kinetic specimens were cast between parallel plates spaced 1/8 inch apart which had been treated with A-156 release agent to facilitate separation. The one-dimensional diffusion specimens which were rods of the same epoxy resin system were vacuum cast into glass tubes with inner diameters ranging from about .07 to .19 inches. The glass tubing was also treated with A-156 release agent. After casting, a cure cycle was used which insured complete cross-linking.

The composite system studied had the above matrix with the reinforcement being continuous unidirectional glass filaments. Composite specimens were made by filament winding twelve layers of PPG 1064 T4 glass. The resulting unidirectionally reinforced epoxy sheet was approximately .125 inches thick. The filament concentration, determined by burn-off, was found to be approximately 56% by volume. The cure cycle used was identical to that of the homogeneous material and assured the complete cross-linking of the matrix material.

Experimental Procedures:

A. Sorption Tests:

The kinetics of benzene sorption by the homogeneous matrix material was obtained by submersing rectangular specimens with approximate dimensions of 1/2" x 1" x 1/8" and round specimens with diameters of .55" in benzene at room temperature (24°C). The depth of penetration and swell

as defined in Figure 1 were measured at increasing time intervals. The measurements were made with a traveling stage optical micrometer with accuracy to .0001 inches.

The composite specimen sorption-kinetics data were obtained by placing rectangular specimens with dimensions about 1-3/4" x 3/8" x 1/8" in benzene at room temperature. The specimens had fiber orientations varying from 0 to 90 degrees at 15 degree intervals as shown in Figure 2. The dilatational measurements were made with both a standard micrometer and the optical micrometer discussed above. The gel-core interface was not a sharp, well defined line as was the case with homogeneous material tests and this necessitated a cross-sectioning of the specimens at increasing time intervals. Characterization of the sorption pattern with varying filament orientation was done visually, and measurements were made with a Stereo-Scan microscope having a vernier eyepiece.

B. One-dimensional Diffusion Tests:

The one-dimensional diffusion tests utilized cylindrical specimens with very small diameters (.07 - .193 inches). The organic solvent (in this case benzene) was allowed to diffuse into the rod through one end only with the other end being free to move. The rate of diffusion of benzene down the length of the rod was measured with the travelling stage optical micrometer. Figure 3 is a schematic of the experimental set-up used in this study. As is shown in the schematic, glycerine was used to assure the sorption of benzene only at the rod end. The amount of rod end exposed to the benzene environment could be accurately set through the use of the adjusting screw. These experiments were conducted at room temperature.

RESULTS AND DISCUSSION

The primary objective of this research was to characterize experimentally the sorption of benzene by a unidirectional glass filament-reinforced epoxy composite system. The effect that filament orientation has on the rate and mode of sorption was of particular importance in the study. The conventional Fickian description for diffusion in an anisotropic media is

$$-F_1 = D_{1j}C_{,j} \quad (1)$$

where F_1 is the flux in the l th direction; D_{1j} is the second order diffusion coefficient; and $C_{,j}$ is the gradient of the concentration in the j th direction.

This research program was conducted to determine if the sorption kinetics in our composite system could be represented by a formulation such as equation (1). If this were the case, then principal diffusion coefficients could be found which would correspond to the principal axis of the material. Knowing the principal coefficients, the coefficient in any arbitrary direction can be expressed as

$$D_N = l^2 D_1 + m^2 D_2 + n^2 D_3 \quad (2)$$

where D_1 , D_2 , and D_3 are the principal coefficients and l , m , and n are the direction cosines relative to the principal axis of diffusion.

Figure 4 is a schematic which illustrates the gel-core area distributions as observed in cross-sections of specimens with varying filament orientations taken at increasing time. The profound influence of filament orientation on the mode and rate of sorption is strikingly evident.

From the experimentally observed sorption characteristics of the system as shown in Figure 4, the existence of two competing phenomena is clear. These two phenomena are: first, an increase in the rate of sorption through channeling, etc. with decreasing difference in the angle between the flux direction and filament direction; second, a reduction in the rate of sorption

of benzene which results from severe restraint on the matrix dilation by the filaments and the corresponding large internal stresses. The effect of the second mechanism increases as the filament direction approaches the flux direction. Summarizing, the sorption of benzene in our composite system should be at a maximum at a filament orientation between 0 degrees, which should have the fastest rate of sorption but which also has the most restraint to swelling, and 90 degrees which has the slowest rate of sorption, but also the least restraint to swelling. Figure 4 shows this to be exactly the case.

In Figure 4, both (a) and (b) show no evidence of sorption of benzene at the midpoint ($y = 0$, Figure 2) of the cross sections for filament orientations less than 45 degrees at time intervals of 24 and 48 hours. Whereas, at orientations of 45 degrees and greater, evidence of sorption into the cross section at the midpoint is observed at the same time intervals.

As the ability to dilatate increases within a specimen, that is, as we move toward the top and bottom of the specimens, an increase in the depth of penetration is observed. The slope of the gel-core interface at the corners of the cross sections is an indication of the interaction between the effects of filament orientation on both sorption and dilatation. A plot of the angle ϕ which is used to represent the slope versus filament orientation is presented in Figure 5. The extreme dependence of the slope on filament angle is apparent. From the above discussion, it can be concluded that formulations such as Equation (1) cannot be used to describe macroscopic sorption characteristics in our composite system. In other words, a unique second order tensor D_{ij} which describes sorption in our system does not exist.

To further understand the sorption mechanisms resulting in the observations discussed above, additional work was conducted to characterize the

sorption kinetics of the pure epoxy resin and to determine the effect internal stress would have in modifying the rate of sorption.

The characterization of the sorption kinetics of benzene by the homogeneous epoxy resin has been completed. The experimental results obtained during this phase have been discussed in a previous paper [1], and the type of sorption observed where the rate of penetration is constant has been designated Case II diffusion by Alfrey et al [2]. Case II is the limiting case of anomalous diffusion. The observation that the sorption-kinetics are described in this way (i.e. non-Fickian) is not surprising in view of the fact that the material system is highly cross-linked. Other workers have shown that the amount of variation from classical "Fickian" behaviour increases as the degree of cross-linking increases.

The measurement of depth of penetration with time was simplified as a result of the presence of a sharp gel-core interface. This sharp interface has been observed previously in other systems such as epoxy-benzene by Kwei [3] and 5% DVB/95% Styrene-MEK by Alfrey [2]. An important fact which will be used later in this paper is that the concentration gradient for a sharp gel-core interface system and Case II diffusion has been found to be very steep. The equilibrium swell ratio, i.e. the ratio of the equilibrium gel dimension to the unexposed resin dimension, has been determined to be 1.17.

The extreme importance that restraining the matrix swelling (inducing internal stresses) had in reducing the amount of sorption has been discussed above. The one-dimensional diffusion experiment discussed earlier was conducted to characterize quantitatively the effect of stress on the sorption kinetics. The results of the experimental aspect of this phase are shown in Figure 6 where the depth of benzene penetration down the rod is plotted as a function of time for five different rod diameters. The rate of penetration was found to increase as rod diameter increased. For comparison, the rate of

penetration observed in the two-dimensional experiment is also plotted. It should be noted that the use of the one-dimensional experiment approach allows sorption studies to be conducted for extended periods of time (>3000 hours) without the presence of cracking. With the conventional two-dimensional specimen geometry, the swelling stresses generated result in stress cracking after short periods of time.

An analysis of the stress state within the .07, .131, and .191 diameter rods was made for one finite time after exposure. This analysis was conducted to verify the assumption that the underlying cause for the differences in sorption rate was that of the effect of stress. It should be noted that the analysis of stress is for the elastic solution and this fact may introduce some error. Work is currently being conducted to obtain a plastic solution.

The method of analysis used to determine the stress state was that of the finite element method called Structural Analysis of Axisymmetric Solids (SAAS II) [4]. This program has been used in the aerospace industry to perform the stress analysis of complex axisymmetric structures subjected to thermal and mechanical loads. In our analysis, the state of stress (elastic case) in the rod in the gel-interface region was assumed identical to that which existed in a homogeneous bar subjected to a step thermal gradient. This assumption was partially based on previous work [2,5] which showed that for Case II "anomalous" diffusion, the swollen gel is essentially in an equilibrium state of swelling.

To make the thermal problem analogous to that of the one-dimensional diffusion case, the material properties of the heated and ambient sections of rod were matched with those of the gel and core, respectively. The computed stress - both the hydrostatic and deviatoric component in the axial (z) direction - in the core at the gel core interface are shown in Figure 7 for the elastic solution. If one looks only at the deviatoric stress component

the rate of diffusion is seen to increase with an increase (less negative) stress in the direction of the flux. It has been noted by other workers that, based on experimental observations, stress transverse to the flux direction does not appear to modify Case II sorption rates, whereas, tensile stresses in the direction of the flux theoretically should increase the rate of transport.

CONCLUSION

This research effort has revealed the presence of competing mechanisms which control the rate and mode of sorption of benzene by the composite system. Therefore, equations similar to equation (1) cannot be used to describe sorption of benzene by the composite system. The importance that internal stress has in determining the rate of sorption has been shown through the use of the one-dimensional diffusion experiment. The analysis of stress using a finite element method (elastic solution) has shown an increase in deviatoric tensile stress in the direction of the flux increases the rate of sorption.

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- Figure 5.** Effect of Filament Orientation on Sorption Interaction Angle.
- Figure 6.** Results of The One-Dimensional Diffusion Tests.
- Figure 7.** Axial Stress (Elastic Case) in One-Dimensional Diffusion Experiment.

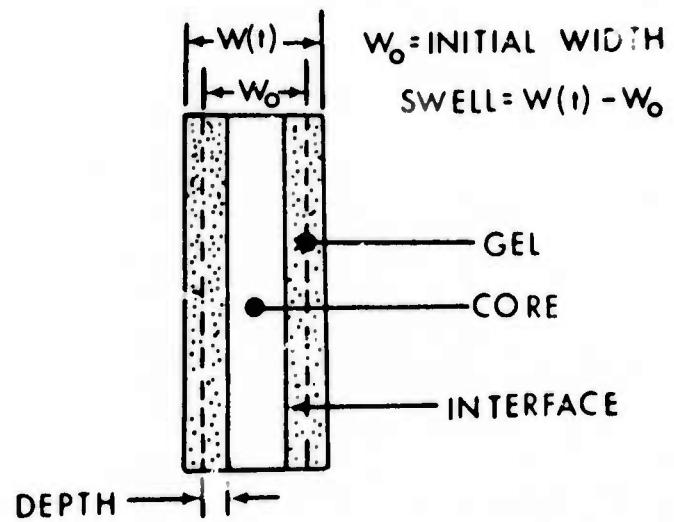


FIGURE 1. SCHEMATIC OF HOMOGENEOUS SORPTION EXPERIMENT.

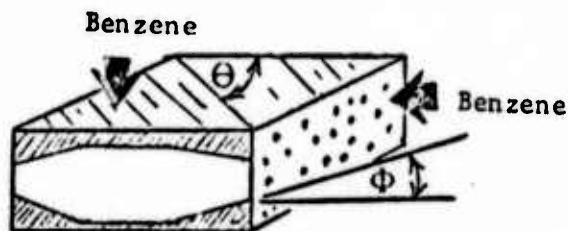


FIGURE 2. SCHEMATIC OF COMPOSITE SORPTION EXPERIMENT.

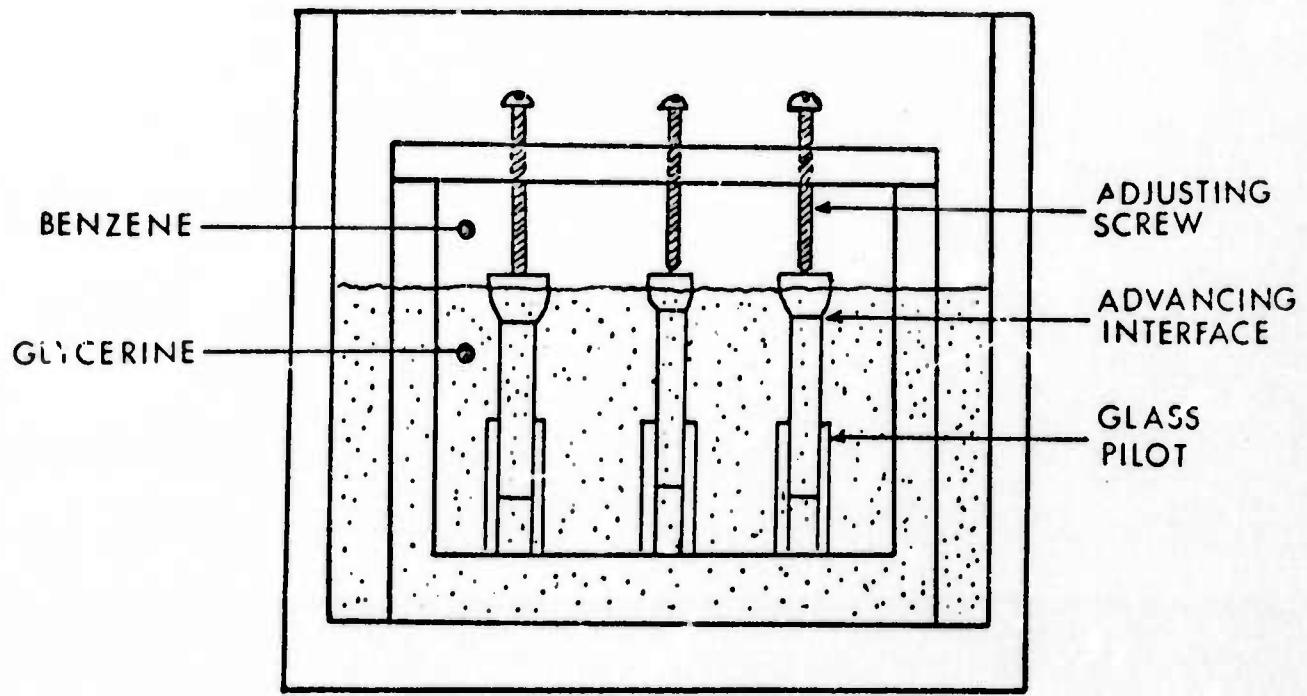


FIGURE 3. SCHEMATIC OF ONE-DIMENSIONAL DIFFUSION EXPERIMENT.

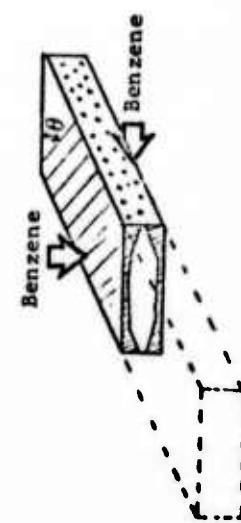
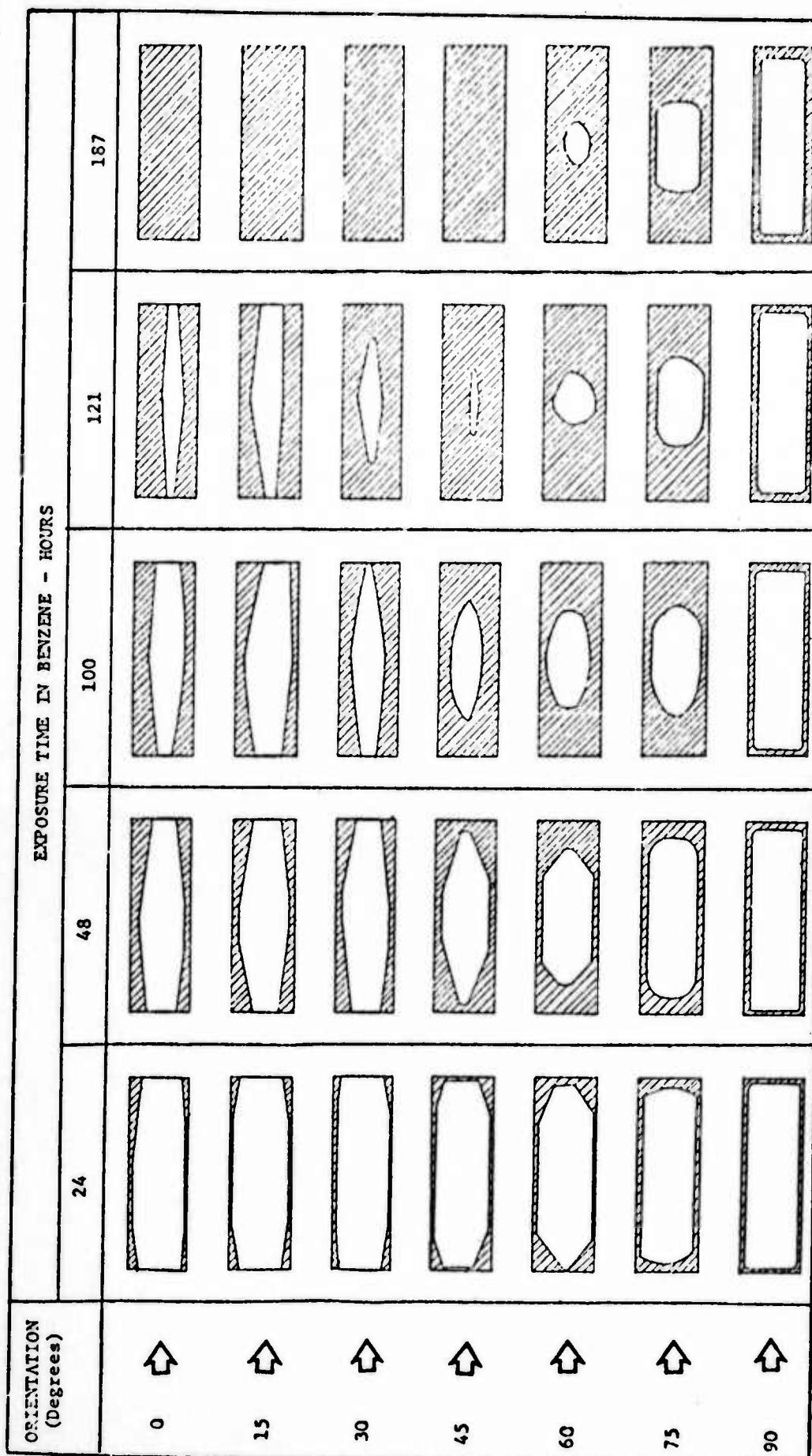


FIGURE 4. RESULTS OF COMPOSITE SORPTION TESTS.

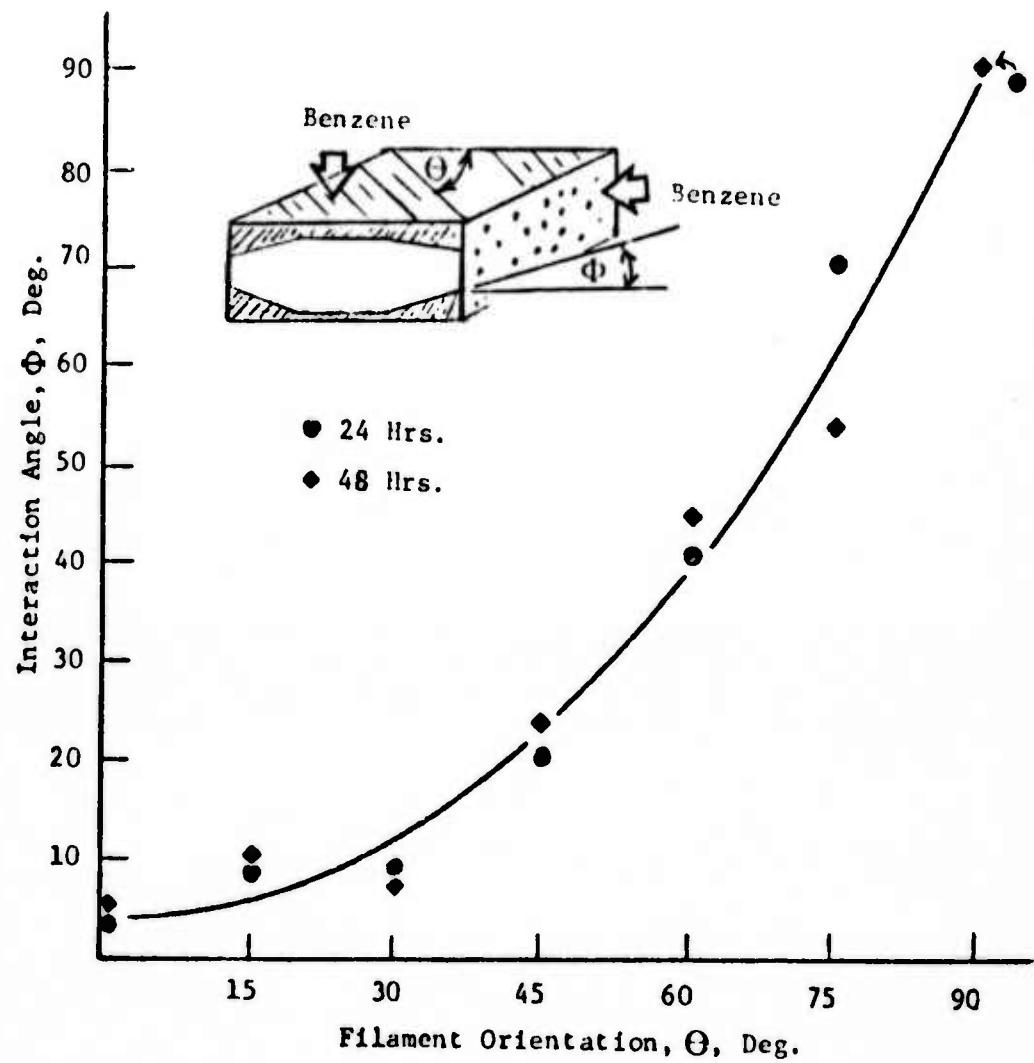


FIGURE 5. EFFECT OF FILAMENT ORIENTATION ON SORPTION INTERACTION ANGLE.

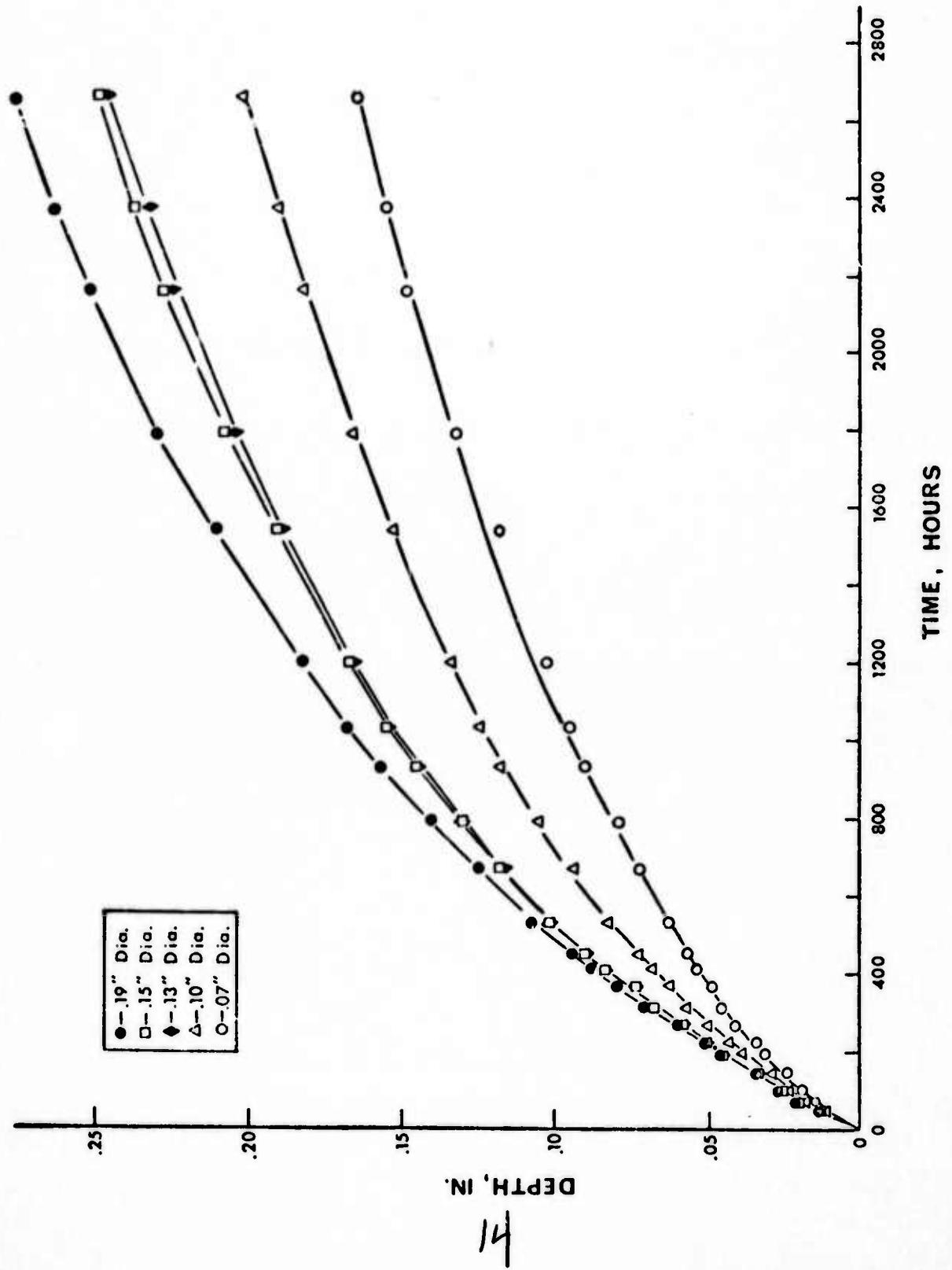
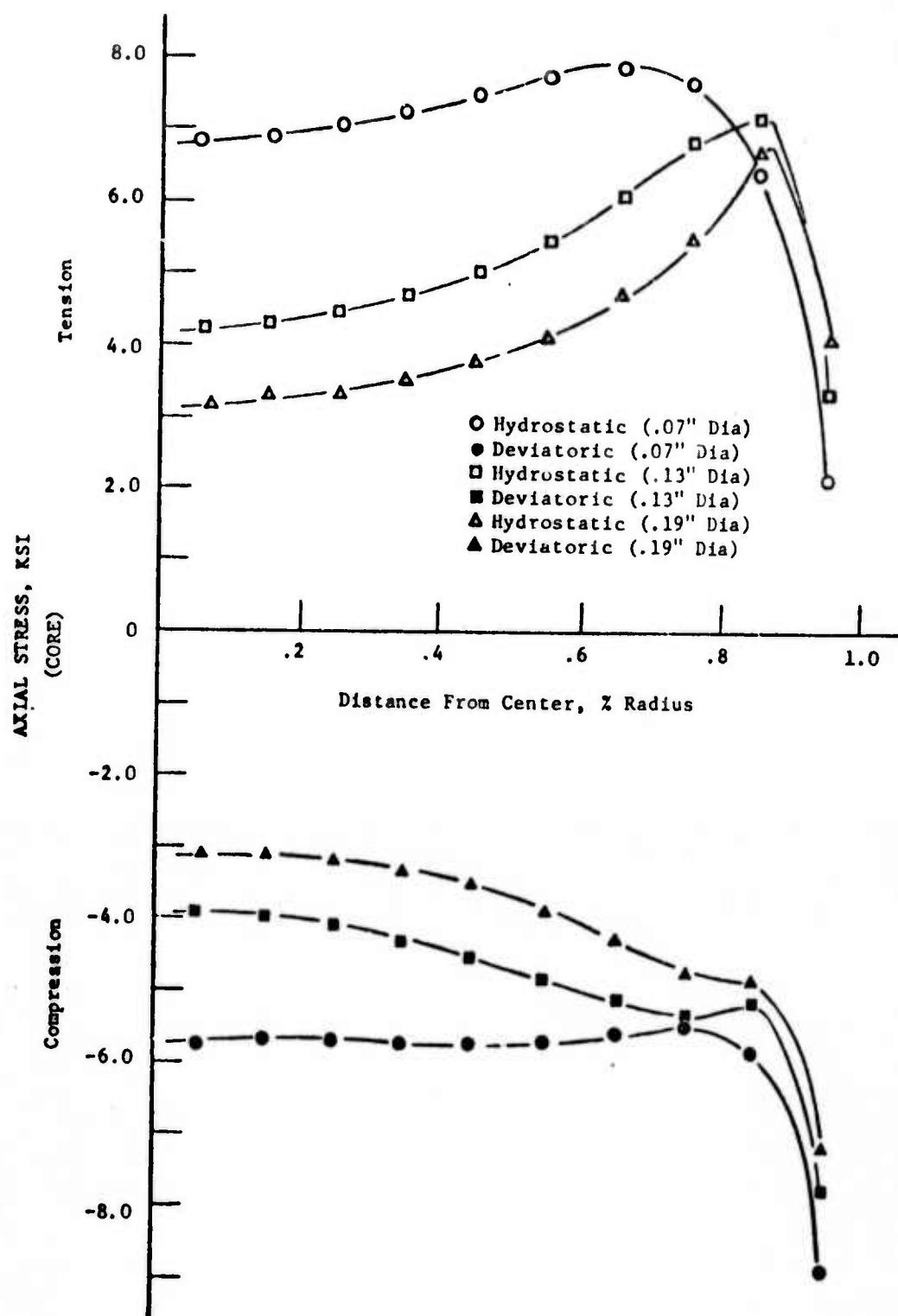


FIGURE 6. RESULTS OF THE ONE-DIMENSIONAL DIFFUSION TESTS.



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FIGURE 7. AXIAL STRESS (ELASTIC CASE) IN ONE-DIMENSIONAL DIFFUSION EXPERIMENT.